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Secrets of Spectroscopy Revealed

SLA

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- 1) I have been a librarian for 2 years at the University of Rochester and I have inherited an excellent collection. I want to keep it up to date, so I volunteered to speak about spectroscopy to enhance my understanding of the subject and learn about new resources.

Outline

- Definitions
- Specific Techniques
- Spectroscopy Resources

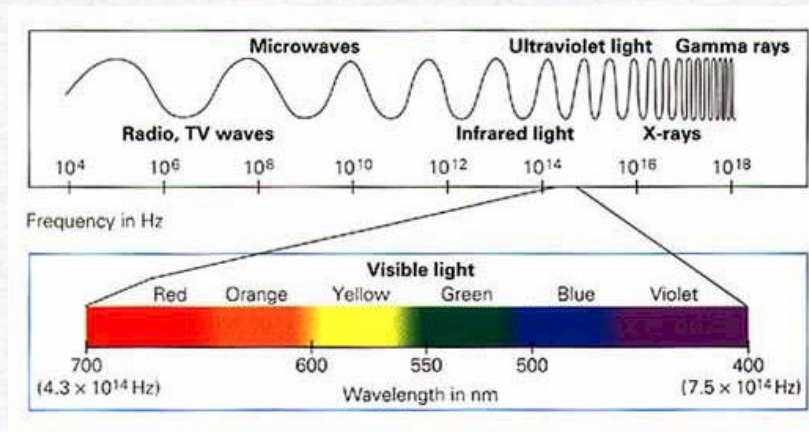
1) Today I want to pass on my learnings. Hopefully there will be something for everyone. I will provide some definitions especially for those new to this subject, I will discuss a few common techniques, and I will talk about resources that you may have for your library. My handout covers vendors and their contact information for the resources I will be discussing.

What is spectroscopy?

A method used to identify and/or quantify
elements, atoms, molecules, matter, molecular
structure
by observing absorption, emission or
scattering interactions
with electromagnetic radiation ("light")

1) So what is spectroscopy? This is my definition derived from several sources, mainly Hawley's Condensed Chemical Dictionary. SLIDE I had to laugh at one web site that I discovered on the history of spectroscopy. The first event was God Said "let there be light".

What is electromagnetic radiation?



From http://www.princeton.edu/~ehs/laserguide/section_1.htm

- 1) But light is really the core of spectroscopy. Hard to describe what it is – but if you can see, you know it is there. Scientists call it electromagnetic radiation, and have described it as waves with electric and magnetic components. They include not only visible light, but slow & wide radio waves and fast and narrow gamma rays.

Electromagnetic Radiation

Equation: $C = v \lambda$

- ☛ Speed of light, $C = 3 \times 10^{10}$ cm/sec
- ☛ Frequency, v = cycles per second in Hz
- ☛ Wavelength, λ = distance between adjacent wave crests in cm
- ☛ Wave number, W = inverse of Wavelength in cm^{-1}

1) They use the length of a wave, or wave length, and cycles per second, or frequency to identify types of light. Frequency and wavelength are related because no matter what type you are talking about, it travels at the same speed, C , the speed of light.

Typical interactions

- Absorption (Absorbance, Transmittance)
 - “light” goes in, doesn’t come out
- Emission (flame, spark, ICP)
 - “light” is given off
- Scattering (Raman)
 - path of “light” is different than what went in, frequency may be different too

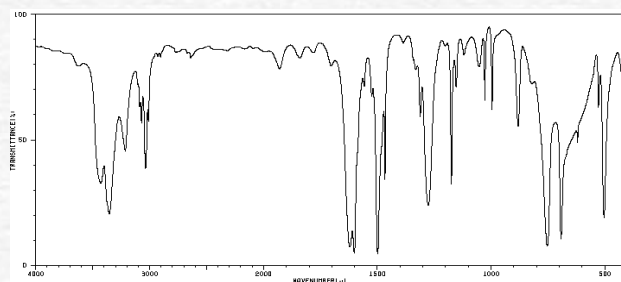
- 1) In spectroscopy, light interacts with samples in three ways:
- Absorption. Light goes into the sample, but doesn’t come out.
 - Emission. Light is given off.
 - and Scattering. Light goes through the sample, but is changed and comes out at a different path and often a different frequency.

What is a spectrum?

- Graphical representation of what is happening to the electromagnetic radiation.

- Ex. Infrared Spectrum (Aniline)

• X: wavenumbers, y: transmittance



From SDBS: Integrated Spectral Database System

1) A spectrum is a graphical representation of how the sample and the light are interacting. Here is an Infrared Absorption spectrum. It shows wavenumbers, which are $1/\text{wavelength}$. Transmittance, which is related to absorbance. Chemists learn information about the structure of a compound by interpreting the spectra because each compound has a unique spectra, sort of like a finger print.

Some common techniques

- MS (1940s)
- Raman (1930s/1960s)
- UV/Vis (1941)
- IR (1951)
- NMR (1952)

1) There are so many techniques in spectroscopy, that I could spend the whole afternoon telling you about them. I have chosen 5 common ones, Mass spectrometry, Raman Spectroscopy, Ultra Violet/ Visible Spectroscopy, Infrared Spectroscopy, and Nuclear Magnetic Resonance Spectroscopy. The date beside them gives you an idea of when these techniques came into acceptance. Generally the data that you might find prior to the 40s and 50s will be of questionable quality. Because of many advancements in techniques in the 60s and 70s the best data can be found in the last 30 years.

Mass Spectrometry (MS)

Ionization and fragmentation of molecules by **high energy electrons in an electric field** used to determine molecular weight

Key Parameters:

ion abundance (intensity)

mass-to-charge ratio (m/e or m/z)

base peak

molecular ion (M^+)

- 1) Mass Spectrometry is not a spectroscopy technique, but I am telling you about it because Mass spec spectra are often bundled with other spectra in the resources. Mass Spectrometry involves the SLIDE

Raman Spectroscopy

Scattering of Infrared light due to molecular bond vibrations.

Key Parameters:

peak location

peak shape

peak strength

wave numbers

transmittance

- 1) Raman Spectroscopy involves SLIDE

Ultraviolet/ Visible Spectroscopy (UV/Vis)

Absorption of Ultraviolet and Visible light due to electrons moving to higher energy levels

Key Parameters:

molar absorptivity (ϵ)
extinction coefficient

maximum absorption (λ_{max})
absorbance

- 1) Ultraviolet/ Visible Light Spectroscopy, often call absorption spectroscopy, involves SLIDE

Infrared Spectroscopy (IR)

Absorption of Infrared light
due to molecular bond
vibrations.

Key Parameters:

peak location

peak shape

peak strength

wave numbers

transmittance

- 1) Infrared Spectroscopy, often used by students in organic lab, involves
SLIDE This type of spectroscopy is related to Raman spectroscopy because it
uses the same frequencies of light and the information gathered is
complimentary.

Nuclear Magnetic Resonance (NMR)

Absorption of radio waves in the presence of a strong **magnetic field** used to determine molecular structure

Nucleus types: **H, C, F, P, N**

Key Parameters:

chemical shift: δ (delta), τ

frequency: ppm or Hz

coupling constant

integrals

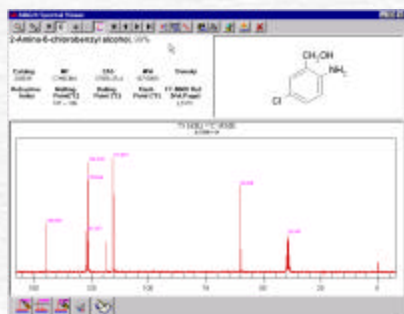
- 1) NMR is an extremely popular and well developed technique. It involves SLIDE Two dimensional NMR, COSY, HETCOR and NOESY spectra have achieved acceptance within the last 15 years.

Library Resources for Spectroscopy

- ✓ Indices to Articles
- ✓ Handbooks
- ✓ Spectra Libraries & Software
- ✓ Encyclopedias & Texts
- ✓ Web Sites

1) Switching subjects here, much information has been recorded about spectroscopy. A primary source is articles so I will tell you how to find them. Data from experiments has been recorded in handbooks and spectra libraries. In fact, there has been a huge effort to record spectra systematically. Special software for capturing, comparing, manipulating, and reporting spectra has been developed. The accuracy and ease of spectra prediction is improving. Lastly, I want to share selected resources useful for learning: encyclopedias, text books and web sites.

Graphs, text and tables



“ ^1H NMR (CDCl_3)
d 3.24 (s, 3H, CH_3N)”

from J. Org Chem V59
(1994) p 479

spectra: graph
From Sigma-Aldrich

articles & handbooks:
text and tables

1) Much of spectroscopy information is recorded in graphical form, a spectra. This is the format that is used in spectral libraries, sometimes articles. However, most articles contain spectral info in text or table form – very cryptic unless you know the code. In this example, the author from the J. Org. Chem article is talking about proton NMR, the solvent is CDCl_3 , the shift, $\delta = 3.24$, the peak is a singlet and represents 3 hydrogens in the CH_3N part of the molecule.

How to find spectroscopy articles

- Chemical Abstracts
- Beilstein/ Gmelin
- Special Indices

Chemical Abstracts, Beilstein, and Gmelin via Crossfire and some other indices are wonderful tools for finding articles.

Spectra info in Chemical Abstracts

- ☞ Search for chemical substance, then limit references to spectral properties (1967+).
 - ✳ In Scifinder Scholar, analyze by index term
- ☞ Older data (pre-1967) do a topic search on substance name and refine by technique and by range of years
- ☞ To enhance STN searches use the STN Lexicon to determine appropriate vocabulary
 - ✳ =>e spectroscopy+kt/ct

In Chemical Abstracts -- SLIDE

Scifinder Scholar: limit substance refs to spectra



Here is the Scifinder Scholar screen that allows you to limit substance references to spectral properties.

Spectra Info in Beilstein/ Gmelin

- ☞ Look up substance of interest and use “field availability” to navigate to spectra references
- ☞ Use the easy data search (EDS) screen for spectroscopy.
- ☞ Combine EDS search with structure or fact editor searches.

In Beilstein or Gmelin -- SLIDE

Field Availability



Here is the Field Availability screen in Beilstein. Depending on what compound you are looking at, you can get references to articles about various spectroscopy techniques by double clicking on your choice.

Beilstein EDS Screen

Spectral Data

Use this form to search for Spectral data

Spectra:
☐ Find all compounds with any spectral data
or specify:
☐ NMR ☐ ESR ☐ IR ☐ UV ☐ MS

or search for specific data on spectra:

- Nuclear Magnetic Resonance:
specific nuclei: in sol.:

- Electron Spin Resonance:
specific nuclei: in sol.:

- Infrared Spectroscopy:
in solvent:

- Ultraviolet Spectroscopy:
with Abs. maxima: in sol.:

OK Help Cancel

Here is the Easy Data Search screen in Beilstein – Gmelin has a similar one.

Useful Indices

- ✓ Chapman & Hall/CRC's "Combined Chemical Dictionary" or "Dictionary of . . ."
- ✓ Hershenson's "Infrared Absorption Spectra" (Academic Press: 1953) & "Nuclear Magnetic Resonance and Electron Spin Resonance" (Academic Press: 1965)

Sometimes you can get false hits when using Chemical Abstracts. When you look up compounds in the Combined Chemical Dictionary, you get references to NMR and IR spectra too, and these tend to be right on. This is the case with the whole set of books that Chapman and Hall have put out that start with "Dictionary of . . ." (Organic, or Organometallic for example). Often they have references to Aldrich's spectral libraries. If you are looking for older spectra, IR or NMR, I have found Hershenson's books to be useful.

Handbooks with Spectral Data

- ✓ Chapman & Hall/CRC's Properties of Organic Compounds
- ✓ Handbook of Data on Organic Compounds (CRC Press: 1994)

If you want to get your hands on NMR or IR data right away for common organic compounds, Properties of Organic Compounds and the Handbook of Data on Organic Compounds are very useful.

Major Spectra Libraries & Software

- ✓ SDBS: Integrated Spectral Data Base
- ✓ Sigma-Aldrich
- ✓ ACD Lab
- ✓ NIST Web Book
- ✓ BioRad's – KnowitAlltm/HaveitAlltm
- ✓ Wiley Chemical Concepts - SpecInfo

Sometimes textual data is not enough. Students especially want to visualize what is happening. Researchers want to manipulate, store or predict spectra. Here are several prominent databases and software. These are available electronically.

SDBS: Integrated Spectral Data Base

<http://www.aist.go.jp/RIODB/SDBS/menu-e.html>

- Size: 47,300 IR; 20,500 MS, 13,700 HNMR; 11,800 CNMR; 3,500 Raman; 2,000 ESR
- Search by: organic compound name; molecular formula, CAS RN; number of atoms of C, H, O, N; chemical shift (^1H and ^{13}C).
- Feature: Can see proton identification with HNMR.
- Most spectra measured at National Institute of Advanced Industrial Science and Technology in Japan.
- Free but limited. See site: notify if many downloads

SDBS is on the web. It is a medium sized collection of IR, MS, NMR, Raman, and ESR spectra. There are several ways to search SLIDE. I really like the proton identification – correlating the spectrum with the structure. Most spectra are measured SLIDE. It is free within their guidelines. Notify them if you will be doing many downloads or they will block your access.

Sigma-Aldrich Print

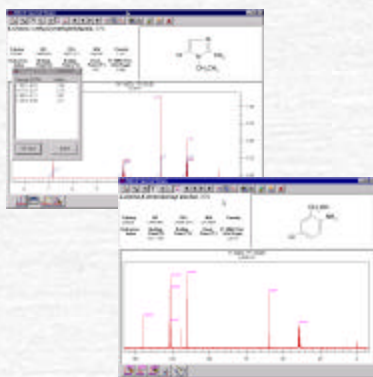


Sigma-Aldrich Reference Books

- 3-Volume sets of spectra
 - ✓ ^{13}C and ^1H NMR spectra for over 12,000 compounds
 - ✓ IR spectra for over 18,000 compounds
- Also available in electronic formats

I have these Aldrich books in my library. They contain a small number of commonly used compounds. My students use them so heavily that we need to rebind them every year.

Sigma-Aldrich CD

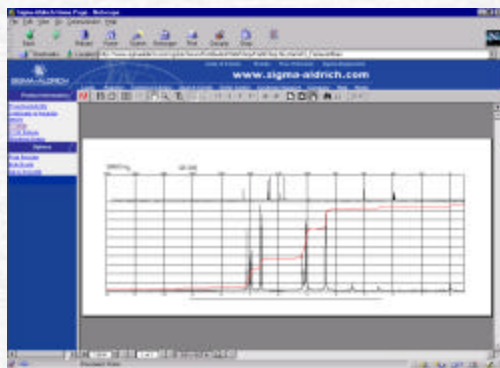


Aldrich Spectral Viewer Software

- HNMR and CNMR for 15,300 Compounds
- Easily searchable
- Includes structures & technical data
- Ideal for:
 - ✓ Comparison studies
 - ✓ Identification of unknown compounds
 - ✓ Teaching spectral interpretation

I find this CD of NMR spectra very exciting. Even though CD-ROMs are old technology, the searching is a great enhancement over the books. You can search by melting point, boiling point, as well as compound name, molecular formula and CAS Registry number. SLIDE If installed on a computer with internet access, you can link directly to the Sigma Aldrich web site ...

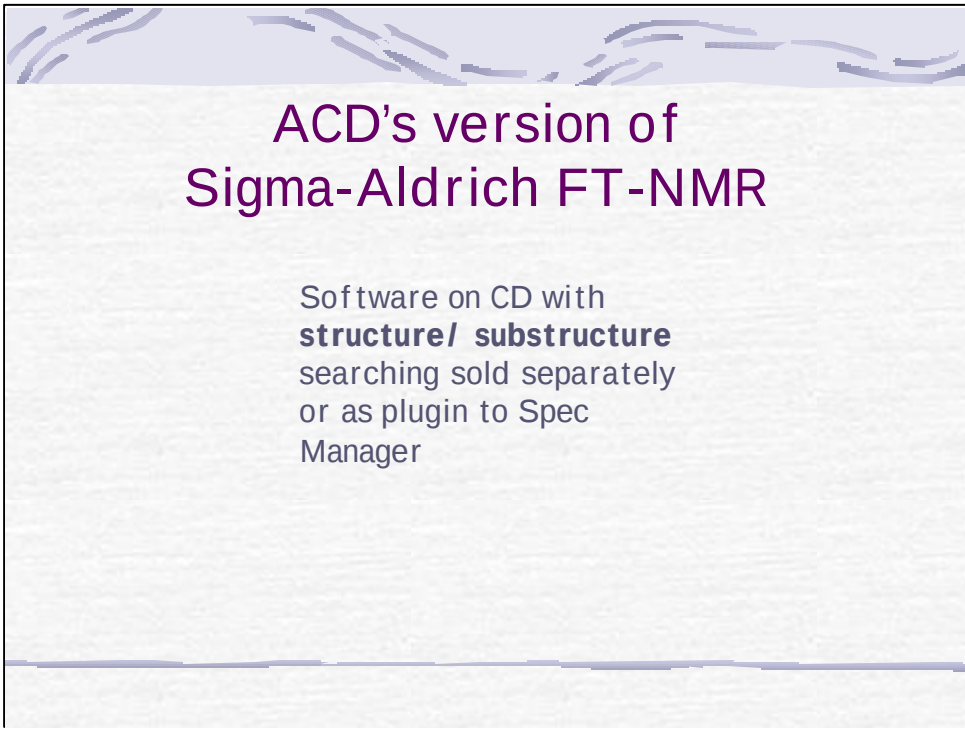
Sigma-Aldrich Web Site



www.sigma-aldrich.com

- Free access to thousands of NMR and IR spectra
- Also available:
 - ✓ Physical properties
 - ✓ Material Safety Data Sheets (MSDS)
 - ✓ Certificates of analysis

where there is free access to IR spectra. By itself, the web site is a gem because there is free access to other physical properties, MSDS sheets and structures.



ACD's version of Sigma-Aldrich FT-NMR

Software on CD with
structure/ substructure
searching sold separately
or as plugin to Spec
Manager

ACD Labs now provides a version of Aldrich's C13/ FT-NMR collection that is structure searchable. If you like, you can get it as a plugin to their Spec Manager.

ACD's Spec Manager

- Software (CD) for processing multiple spectra techniques (NMR, MS, UV-Vis, IR, Raman, GC, HPLC)
- Take raw data from spectrometer, process and store with experimental parameters.
- Search by: structure, substructure, shift, name of compound, user defined fields
- May assign structures using ChemSketch and correlate with spectrum peaks
- Single technique modules available: HNMR, UV-IR, MS, 2D-NMR Managers

Available on CD, Spec Manager can be used to process multiple types of spectra. Raw data can be imported into software right from an instrument. The user can add structures and whatever additional information they choose. They can then search by SLIDE.

ACD's HNMR Predictor Software

- ☞ HNMR predictor, also C13, P, F, N
- ☞ Predicts spectra from ChemSketch structure drawing
- ☞ Available on CD or internet via I-Lab product
- ☞ Can be used with NMR Manager
 - Run sample and import into software
 - Draw structures that you think you have
 - Predictor will tell how well the structure and spectra match

ACD is well known for predicted physical properties many listed now in Chemical Abstracts. They also have software for predicting NMR spectra – for proton, C13, F, and N. SLIDE This product could be especially useful to students who are learning spectra interpretation or researchers who are making new compounds.

ACD's HNMR DB Add-on

~122,000 structures

1 million experimental chemical shifts

250,000 coupling constants

Search original references, solvents, frequency,
NMR techniques, MF, MW, IUPAC names, trivial
names

If you like, you can add on a database of structures. These will lead you to the original references with experimental data. They can be searched in traditional ways.

Bio-Rad's KnowItAll™

- Modular / customizable software on CD. Various application options, such as Database Building, available at low cost.
- 4 Editions: Analytical, ChemWindow, Forensic, Student
- Features: Spectra retrieval, manipulation, prediction, interpretation, storage, reports, structure drawing, compound naming
- Search by: spectrum, peaks, compound name, CAS #, MF, MW, structure, substructure, physical properties, chemical properties . . .
- Review in JACS V. 124 (7) 2002 p. 1555

I have sets of green Sadtler binders in my library. The newest version of Sadtler information can be found using BioRad's KnowitAll and HaveitAll products. KnowitAll is the software component on CD. SLIDE It can be used to build an in-house spectra library. It may be purchased for a one time fee.

BioRad's Have It All™

- ✔ >500,000 high quality reference spectra on CD
- 4 major spectra sets
 - NMR: ~12,000 HNMR & ~147,000 CNMR
 - IR: ~230,000 IR & ~3,800 NEAR IR,
 - Raman: ~3,300
 - MS: ~107,000 (NIST)
- ✔ Includes structures and experimental conditions
- ✔ Can build collections for multiple techniques such as UV/VIS, GC, IR, ¹³C NMR, ¹H NMR, Raman, NIR, MS
- ✔ Easy to move between techniques
- ✔ Databases available by subscription

HaveItAll is the database portion of BioRad's offering. They have a very large, high quality spectra collection which includes SLIDE. If you are looking at the data for one compound, it is easy to bring up all the available information, including spectra generated using various techniques.

NIST WebBook

<http://webbook.nist.gov/>

- ☛ Size
 - IR: ~8700 compounds.
 - MS: ~12,000 compounds.
 - UV/Vis: ~400 compounds.
 - Electronic and vibrational spectra: ~4000 compounds.
- ☛ Search by: name, chemical formula, CAS registry number, molecular weight, chemical structure, or selected ion energetics and spectral properties.
- ☛ Part of the Standard Reference Data Program
- ☛ Free

The NIST Web book is another free web resource. It contains a small collection of Spectra. There are many ways to search, including SLIDE.

Chemical Concept's SpecInfo

- ☛ Three products: SpecInfo Inhouse, SpecData, SpecInfo Internet
- ☛ Features: Build an internal database, match spectra, predict NMR shifts: carbon and protons, elucidation, structure drawing, reports
- ☛ Search By: Structure, substructure, chemical name, MW, MF, CAS RN
- ☛ Also available on STN – 194,000 spectra

Another major player in spectra software and libraries is Chemical Concepts, a Wiley company. They have 3 products SLIDE.

Chemical Concept's SpecData

- ☛ >700,000 spectra with 500,000 structures derived from multiple sources
- Includes spectra for 24,000 natural compounds
- Spectra sets:
 - ◆ ~250,000 NMR;
 - ◆ ~340,000 MS;
 - ◆ ~30,000 IR;
 - ◆ and 3,800 NIR spectra.
- ☛ Includes experimental conditions.
- ☛ Databases available by subscription or purchase
- ☛ No user limit.

Spec Data is the largest collection of spectra that I have encountered. This library includes experimental data. You can purchase the whole collection or access it via subscription. There is no user limit.

SpecInfo Internet or Inhouse

Web version

- ☛ Convenient to access
- ☛ Requires SpecSurf XS plugin

Internal installation

- ☛ Increased security
- ☛ Fast Searching
- ☛ Flexibility

For convenient access, you can subscribe to a web version that has a browser plugin. For increased security you can purchase and install the whole database on an internal server for faster searching and more flexible use.

Encyclopedias & Texts

- Wiley's Handbook of Vibrational Spectroscopy (2002)
- Introduction to spectroscopy : a guide for students of organic chemistry / Donald L. Pavia, Gary M. Lampman, George S. Kriz (Thomson Learning: 2001)
- Encyclopedia of Spectroscopy and Spectrometry (Academic: 2000)
- Encyclopedia of Analytical Chemistry (Wiley: 2000)
- Encyclopedia of Spectroscopy (VCH: 1995)
- Practical handbook of spectroscopy / edited by J.W. Robinson (CRC Press: 1991)

See the handout for a listing of newer and useful encyclopedias, texts and internet sites. Some are: SLIDE

Spectroscopy on the internet

- ☛ **Wiley's Spectroscopy Now**
<http://www.spectroscopynow.com/Spy/basehtml/SpyH/>
- ☛ **Web-ster's Organic Chemistry**
<http://ep.llnl.gov/msds/orgchem/spectroscopy.html>
- ☛ **Physics Encyclopedia: Spectroscopy and Radiation**
<http://members.tripod.com/~IgorIvanov/physics/>
- ☛ **Spectroscopy Magazine**
<http://www.spectroscopymag.com/spectroscopy/>
- ☛ **Chemistry Hypermedia Project: Spectroscopy**
<http://www.chem.vt.edu/chem-ed/ac-basic.html>
- ☛ **ACS Division of Analytical Chemistry**
<http://www.acs-analytical.dug.edu/>
- ☛ **Nobel Library Science Reference Room Chemistry Resources**
(Linda Shackle): <http://www.asu.edu/lib/noble/chem/>

SLIDE

Other Interesting tidbits

- Local spectroscopy experts
- Instruments (Perkin-Elmer, Nicolet) with built in libraries
- “Spectral Data” in Protein Databank

Don't feel like you always have to know all the answers. I found a few spectroscopy experts on my campus and I bet your organization has some too. Also note that many instruments are coming with built in spectra libraries. Lastly, be aware that spectral data on the internet may not be what you are expecting. For example, in the Protein Databank, Spectral Data turns out to be molecular coordinates derived from spectroscopy experiments.

Summary

- ☛ observations of the interaction between light and matter
- ☛ many types of spectroscopy and spectra
- ☛ found in articles, reference books, spectral libraries and web sites.
- ☛ specialized software/ database systems for searching, prediction, interpretation, processing, and storage of spectra.

We have covered a lot of ground today. In summary, spectroscopy refers to:
SLIDE

Acknowledgments

- ✓ Conrad, ACD Labs
- ✓ Grace Baysinger, Stanford
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- ✓ Nancy Simons, Georgia Tech
- ✓ Larry Taylor, BioRad Informatics
- ✓ Chris Wozniak, Sigma Aldrich
- ✓ U of Rochester Staff: Especially Katie Clark, Kenn Harper, Tom Krugh, Sadip Sur

I want to acknowledge the following people for all their assistance with my talk. Thank you.